Guide for Handling Engineered Nanomaterials in ERDC Laboratories

ERDC – Engineer Research and Development Center (ERDC),

Environmental Laboratory, Vicksburg, MS

This document is intended to describe voluntary standardized operating practices of the U.S. Army Corps of Engineers Engineer Research and Development Center (ERDC) when working with or otherwise handling engineered nanomaterials. For users other than staff associated with ERDC, this document is for reference purposes only; it is not a citable document.

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Prepared for the US Army Corps of Engineers, Engineer Research and Development Center (ERDC)

http://el.erdc.usace.army.mil/nano/index.html

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Engineer Research and Development Center

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DEFINITIONS

Agglomerate

Group of particles, held together by weak interactions, such as van der Waals forces, electrostatic forces, and surface tension, that are separated relatively easily with mild perturbation [1].

Aggregate

Heterogeneous particle in which various components are not easily separated as they are held together by relatively strong forces [1].

Engineered Nanomaterials

Materials that are intentionally produced to have at least one dimension (e.g., diameter, length) between 1 and 100 nm so as to impart unique properties not observed in materials of larger size.

Environmental Health and Safety

In the context of this document, Environmental Health and Safety (EHS) broadly refers to a general class of issues or risks that relate to the health and safety of humans or the natural environment.

Environmental Protection Agency (EPA)

Established in 1970 to protect human health and the environment, the EPA is the nation's lead federal agency dedicated to environmental science, research, education and assessment efforts [2].

High Efficiency Particulate Air

Describes a type of filter designed to remove sub-micron particles from contaminated airstreams with high efficiency.

Inhalable

Describes particles that are smaller than 10 micrometers in diameter (10 μm), which can be breathed into the lungs (abbreviated as PM10).

Material Safety Data Sheet (MSDS) (or Safety Data Sheet [SDS])

A compilation of information required under the OSHA Hazard Communication Standard (HCS) on the identity of hazardous chemicals, health and physical hazards, exposure limits, and precautions. Section 311 of SARA requires facilities to submit MSDSs under certain circumstances [3]. The Safety Data Sheet (SDS) is equivalent to the MSDS under the Globally Harmonized System of Classification and Labeling of Chemicals adopted by the United Nations.

Nanotechnology

The study of atomic, molecular or macromolecular phenomena (at an arbitrarily designated length scale of approximately 1 - 100 nanometer), structures, devices and systems that have novel properties and functions because of their small and/or intermediate size [4].

National Institute of Occupational Safety and Health (NIOSH)

As part of the Centers for Disease Control and Prevention (CDC) in the Department of Health and Human Services, NIOSH is the federal agency responsible for conducting research and making recommendations for the prevention of work-related injury and illness [5].

Occupational Safety and Health Administration (OSHA)

Established in 1970, OSHA is the lead federal agency that promotes the safety and health of American workers by setting and enforcing standards; providing training, outreach and education; establishing partnerships; and encouraging continual process improvement in workplace safety and health.

PM2.5

Particulate matter including fine liquid or solid particles such as dust, smoke, mist, fumes, or smog, that are less than 2.5 micrometers in diameter and commonly found in air or emissions [3].

Personal Protective Equipment (PPE)

Equipment, including respirators, specialized clothing, eyewear, hearing protection, and various other protective devices, that are used by individuals to reduce employee exposure to hazards when engineering and administrative controls are not feasible or effective in reducing these exposures to acceptable levels. Employers are required by OSHA to determine if PPE should be used to protect their workers [6].

Ultrafine Particle

Particles of less than approximately 100 nm in diameter.

ACRONYMS

ASTM	American Society for Testing and Materials
BSI	British Standards Institute
DOE	Department of Energy
EDX	Energy Dispersive X-Ray Spectroscopy
EHS	Environmental Health and Safety
EPA	Environmental Protection Agency
GHS	Global Harmonization Standard
HEPA	High Efficiency Particulate Air
HSE	Health and Safety Executive (UK)
MSDS	Material Safety Data Sheet
NIOSH	National Institute of Occupational Safety and Health
NSRC	Nanoscale Science Research Centers (DOE)
OSHA	Occupational Safety and Health Administration
PM2.5	Particulate Matter of less than 2.5 microns in diameter
PPE	Personal Protective Equipment
SDS	Safety Data Sheet
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
ULPA	Ultra Low Particulate Air
UN	United Nations

Overview

This document provides general guidance voluntarily enacted for use by ERDC personnel to minimize environmental health and safety (EHS) risks during the acquisition, use, and disposal of engineered nanomaterials. The document is separated into five general areas illustrated in Figure 1. These five areas are intended to address many of the situations ERDC personnel are likely to encounter when working with engineered nanomaterials. It is recognized, however, that no document can address all such situations and users of this guide may need to seek additional information not contained in this document from other sources (some of which are cited in this document). Further, new developments in the emerging area of nanotechnology EHS may require the periodic modification of information contained herein. Personnel should be aware of the need for such modifications and ensure that their work practices reflect the most recent guidance available.

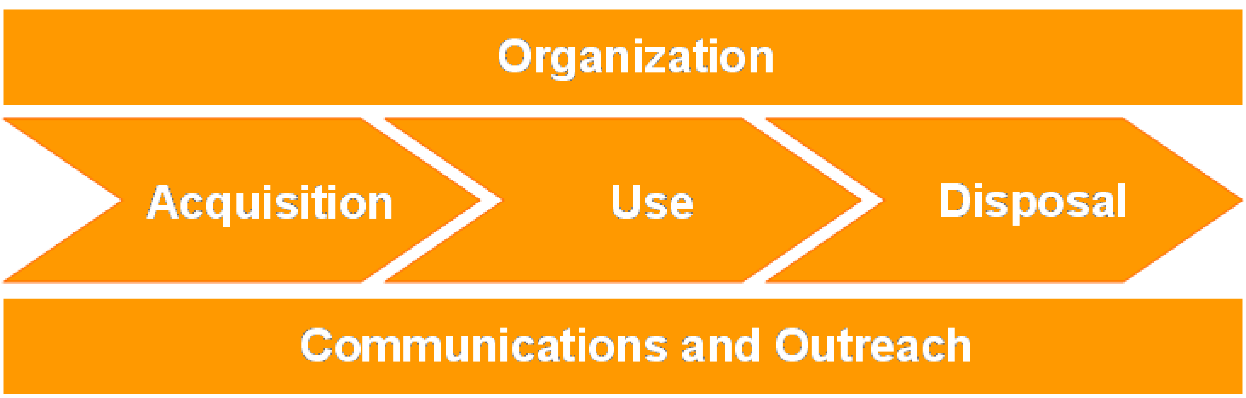


Figure 1. This guidance document provides a comprehensive approach to minimizing nanotechnology EHS risks at ERDC facilities.

Emerging Nanotechnology EHS Guidance

This ERDC framework benefits from and builds upon nanotechnology EHS framework documents established previously by standards bodies, members of industry, and federal laboratories. These documents, which are listed below, offer varying perspectives on identification and management of nanotechnology EHS risks in the laboratory and beyond.

These documents, as well as other relevant resources, have been consulted during the preparation of this SOP.

- **NIOSH Approaches to Safe Nanotechnology: An Information Exchange with NIOSH.** Document published through the US National Institute of Occupational Safety and Health (NIOSH) that *"reviews what is currently known about nanoparticle toxicity, process emissions and exposure assessment, engineering controls, and personal protective equipment."*
  Link: www.cdc.gov/niosh/topics/nanotech/safenano/
- **ASTM Standard Guide for Handling Unbound Engineered Nanoscale Particles in Occupational Settings.** Guide published by the American Society for Testing and Materials (ASTM) that *"covers handling principles and techniques that may be applied, as appropriate, to the variety of [unbound, engineered nanoscale particles—UNP] materials and handling settings."*
  Link: www.astm.org/Standards/E2535.htm
- **Department of Energy Nanoscale Science Research Centers Approach to Nanomaterial ES&H.** Guide published by the Department of Energy (DOE) that *"covers Conceptual Foundations, Controls for R&D Laboratory Operations, Verifying Program Effectiveness, Transportation of Nanomaterials, Management of Nanomaterial-Bearing Waste Streams, Management of Nanomaterial Spills, and an Example Industrial Hygiene Sampling Protocol."*
  Link: www.er.doe.gov/bes/DOE_NSRC_Approach_to_Nanomaterial_ESH.pdf
- **British Standards Institute Document Series.** A series of publications that *"address nanotechnology terminology, health and safety issues, product labelling and materials specification."*
  Link: www.bsi-global.com/en/Standards-and-Publications/Industry-Sectors/Nanotechnologies/
- **NanoRisk Framework (DuPont/Environmental Defense).** A comprehensive document produced through a joint industry/non-profit agency partnership that

provides an *"approach to managing the risks that come with the promise of nanotechnologies."*

Link: www.nanoriskframework.com/page.cfm?tagID=1095

- **NanoSafe Framework.** One of the earliest framework examples established specifically for small- to medium-sized nanotechnology entities engaged in nanotechnology-related manufacturing and research.

  Reference: Hull, M. (2006). "Luna Innovations NanoSafe Framework for Managing EHS Risks." International Conference on Nanotechnology Occupational and Environmental Health & Safety: Research to Practice. Cincinnati, OH.

Background

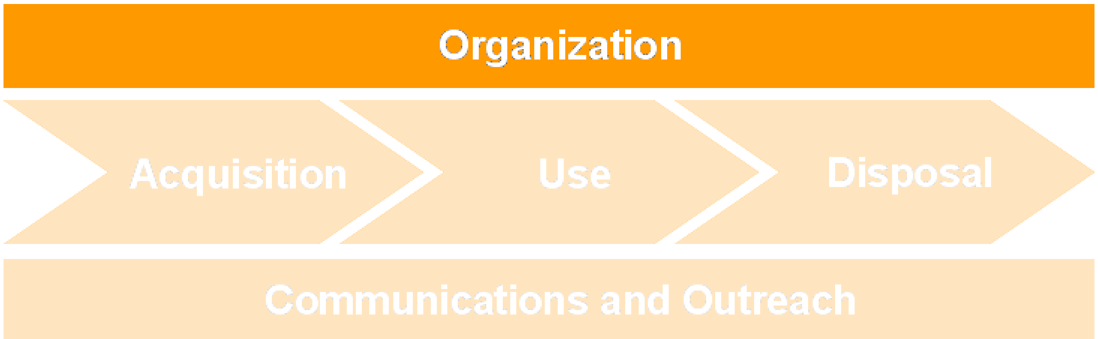
Nanomaterials are materials designed and produced to have structural features with at least one dimension size of 100 nm or less (1nm = 1.0 x 10^{-9} m). The physical, chemical and biological properties of the nanomaterials are different than those of individual atoms and molecules of micron or larger sized materials [7] and consequently the behavior of nanomaterials is unpredictable. The potential hazards with nanoparticles are associated with dispersed and isolated particles more than those integrated into products and devices. Although knowledge on the safety of nanomaterials (exposure assessment, toxicity thresholds, test schemes, etc) is limited [7], their potential routes of exposure to humans are inhalation, ingestion, dermal and injection ([8-12]). The inhalation route is potentially the most important and depends on degree of aggregation of the material in the air.

The changes in temperature, pressure, humidity or electrostatic charge among other environmental variables can alter the stability and properties of nanomaterials. Changes in the properties of the materials might change their reactivity in the environment [13] thus making it difficult to predict their stability and reactivity with living systems.

Given the limited information available on safe handling of engineered nanomaterials, interim guidance is needed to advise personnel of work practices that, based on the synthesis of currently available information, may help reduce EHS risks to a manageable level.

Purpose

This Standard Operating Procedure (SOP) outlines voluntary procedures for mitigating risks during handling, storage and use of engineered nanomaterials in laboratories and to avoid unintended releases to the ambient environment. The SOP should be used in conjunction with the Material(s) Safety Data Sheets (MSDS) from the suppliers of the nanomaterials.



<u>Organization.</u> The following summarizes SOPs for the organization of nanotechnology EHS risk management activities at ERDC facilities.

In this section:

- ☐ Overview
- ☐ Management Commitment
- ☐ Nanotechnology EHS Committee Formation
- ☐ Nanotechnology EHS Facility Management Plan
- ☐ Action Items

Overview

Emerging guidelines for minimizing nanotechnology EHS risks emphasize the importance of management commitment, a coordinated organizational strategy, and planning. This section provides general guidance on developing and implementing an organizational framework conducive to successful identification and mitigation of emerging nanotechnology EHS risks in ERDC facilities.

Management Commitment

Development and implementation of an organizational nanotechnology risk management program first requires the full commitment and support of top-level managers. In accordance with ASTM E2535 [14], *"A formal, written management policy should be established committing to minimizing potential occupational* [unbound engineered nanoscale particles—UNP] *exposures to levels that are as low as is reasonably practicable."*

Nanotechnology EHS Committee Formation

To carry out the commitment of top-level management to nanotechnology safety, a Nanotechnology EHS committee should be formed to coordinate the identification and management of nanotechnology EHS risks at ERDC facilities. The formation of such a committee is consistent with organizational and personnel recommendations made by standards development bodies (e.g., ASTM), members of industry (e.g., NanoRisk Framework, NanoSafe Program) and federal laboratories (e.g., Department of Energy Program). Activities of the committee may include those listed in Table 1.

Table 1. Example responsibilities of a Nanotechnology EHS Committee.

i)	Regular meetings to discuss nanotechnology EHS concerns and strategies
ii)	Attendance and presentations at nanotechnology EHS conferences and symposia
iii)	Inter-departmental exchange of nanotechnology EHS information
iv)	Revision of laboratory safety SOPs pertinent to nanotechnology EHS
v)	Collection of survey data on potential nanotechnology EHS risks in the laboratory
vi)	Coordination of internal briefings on nanotechnology EHS issues
vii)	Development of a facility nanotechnology EHS plan

The EHS Committee shall be composed of representatives from major organizational groups within ERDC. The Committee may include both federal and contract employees, and represent a range of personnel who are involved with or otherwise knowledgeable in the acquisition, handling, and disposal of engineered nanomaterials at ERDC facilities. The Committee may be comprised in a manner similar to Table 2.

Table 2. Example composition of a Nanotechnology EHS Committee.

i)	**Laboratory researcher** Individuals that routinely handle or otherwise work with engineered nanomaterials in the laboratory.
ii)	**Safety and health personnel** Individuals responsible for facility EHS compliance.
iii)	**Area manager** Individual with management-level authority over a particular team, laboratory, or group of laboratories.
iv)	**Acquisitions manager** Individual tasked with purchasing or otherwise acquiring nanomaterials for use within ERDC facilities.
v)	**Communications facilitator** Individual with specific responsibilities to facilitate communications among organizational units.

The Committee should appoint a chairperson and establish an administrative process to facilitate its activities.

Nanotechnology EHS Facility Management Plan

One of the first tasks of the Committee should be to assemble a comprehensive nanotechnology EHS facility management plan. The plan may include the guidance contained in this document, but should also include pertinent information and procedures linked to ERDC's existing facility EHS management programs. Table 3 lists information that may be included in the ERDC Nanotechnology EHS Facility Management Plan.

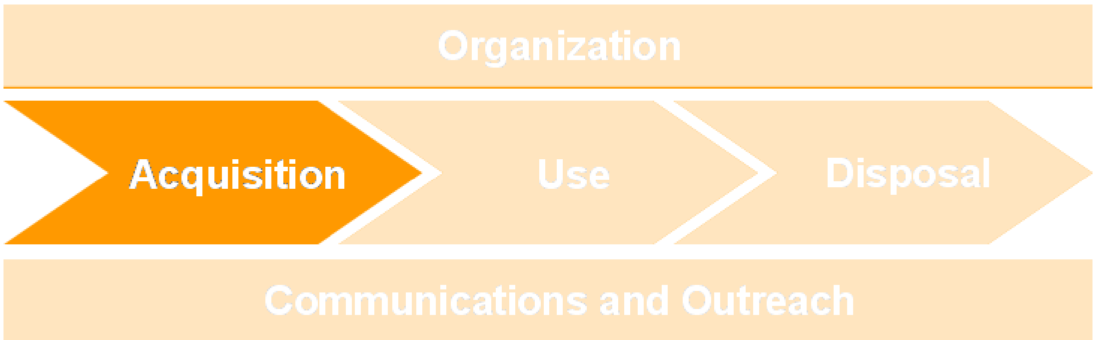
Table 3. Example contents of the ERDC Nanotechnology EHS Facility Management Plan.

▪ ERDC responsible party
▪ Existing facility EHS management program
▪ General guidance for nanotechnology EHS risk management
▪ Collection of SOPs
▪ Pertinent contact information
▪ Contingency plans
▪ Record of major communications
▪ Publications

Action Items

The following summarizes action items from this section:

- ☐ Establish formal, written management policy (e.g., this document)
- ☐ Form Nanotechnology EHS Committee
- ☐ Assemble Nanotechnology EHS Facility Management Plan



Acquisition. **The following summarizes SOPs for the acquisition of engineered nanomaterials at ERDC facilities.**

In this section:

- ☐ Overview
- ☐ Nanomaterials Master Inventory List (NMIL)
- ☐ Minimal Criteria for Externally-Supplied Nanomaterials (ESN)
- ☐ Nanomaterials Prepared In-house (NPI)
- ☐ Characterization of Nanoscale Materials
- ☐ Containment
- ☐ Product Information: Labels and MSDS (or SDS)
- ☐ Shipping
- ☐ Action Items

Overview

Given the early stage of development of nanotechnology, efforts should be made to coordinate the acquisition of engineered nanomaterials through a centralized system or point of contact. This system should apply to externally-supplied materials (i.e., those purchased from commercial suppliers) as well as to those materials synthesized on-site within ERDC laboratories or contract laboratories. An effective acquisitions system can facilitate tracking of nanomaterials usage in ERDC facilities, improve understanding of the nature and extent of workplace exposures, and assist safety managers with identifying and managing nanotechnology EHS risks. This section summarizes general procedures for minimizing EHS risks during the acquisition of engineered nanomaterials.

Nanomaterials Master Inventory List (NMIL)

A master list of nanomaterials acquired by ERDC personnel should be created to document the type, source, quantities, and other pertinent information relevant to engineered nanomaterials acquired and/or stored at ERDC facilities (Table 4). All ERDC personnel and contractors acquiring engineered nanomaterials should contribute information on their acquisitions to the NMIL. The NMIL will be maintained by ERDC materials procurement personnel. The NMIL does not necessarily need to be separate from the conventional chemical inventory list, but it should provide a means for distinguishing engineered nanomaterials from more conventional chemicals. To the extent practicable, ERDC employees in need of nanomaterials (e.g., for environmental studies) may consult the NMIL to determine whether needs can be met with existing materials. Collectively, these efforts will help centralize acquisition of nanomaterials such that the types and quantities of materials held on-site are known.

Table 4. Example fields for inclusion in NMIL entries.

Field	Example Entry
Type	Single-walled carbon nanotubes
Quantity	<10 grams
Source	Carbon Nanotubes, Inc. (include supplier contact information)
ERDC Location	Environmental lab A01
POC	J. Steevens

Minimal Criteria for Externally-Supplied Nanomaterials (ESN)

External suppliers of engineered nanomaterials should provide, at a minimum, the use of robust packaging, appropriate product labeling, accurate MSDS, and other information that can inform an end user of potential hazards associated with the use of products containing engineered nanomaterials. Table 5 summarizes minimum requirements to consider when obtaining engineered nanomaterials from external suppliers.

Table 5. Minimum requirements to consider when purchasing engineered nanomaterials from external suppliers.

1)	Robust packaging (e.g., tightly-sealed containers, secondary containment, use of sorbent materials) suitable for preventing the unintended release of the material
2)	Product labeling and accompanying information sufficient for safe handling, storage, and disposal of the material
3)	Complete and accurate MSDS that identifies the nano-scale nature of the material
4)	Any available characterization information (e.g., composition, particle size, surface area, etc.)
5)	Any available information on toxicity, risk of explosion, or other hazards

Nanomaterials Prepared In-house (NPI)

In some situations, ERDC personnel may choose to prepare engineered nanomaterials in ERDC laboratories using, for example, procedures published in the peer-reviewed literature. These materials, designated here as NPI, should be considered in the same regard as purchased materials and should be registered on the NMIL. Each of these instances should be reviewed to ensure that the appropriate EHS considerations are made in each situation. Table 6 summarizes a three-step procedure that can be used to minimize the EHS risks of in-house preparation of engineered nanomaterials.

Table 6. Three-step procedure to minimize EHS risks of NPI.

Step	Description	Purpose
1. Request	Individual submits request for on-site synthesis of engineered nanomaterials (see requirements below)	To describe nature of synthesis procedure and expected output
2. Review	Request is reviewed internally by relevant EHS personnel	To document and review the request; to understand the level of EHS oversight required
3. Respond	Go/no-go response is generated along with recommended EHS considerations	To allow/disallow the request and ensure EHS risks are minimized

At a minimum, a Request for On-Site Synthesis of Engineered Nanomaterials should contain the following information:

1) Person/department preparing/submitting the request
2) Type of nanomaterial to be prepared and summary of synthesis method
3) References (e.g., SOP) or publications describing the proposed synthesis method and associated safety precautions in greater detail
4) Approximate time-frame over which the synthesis will occur
5) Amount of material expected to be generated over this time-frame
6) Any available hazard information on the expected end products

Characterization of Nanoscale Materials

To the extent practicable, physical and/or chemical properties of all engineered nanomaterials acquired or prepared by ERDC personnel should be characterized extensively. Table 7 lists physical and chemical properties of engineered nanomaterials that ASTM [14] lists as candidates for characterization given their potential to influence toxicity and health. Analytical techniques for measuring these properties are provided.

Table 7. Adapted from ASTM, this table lists properties that ASTM links to assessing the hazard potential of engineered nanomaterials [14]. Example EHS considerations as well as techniques for measuring these properties are included.

Property	Example EHS Consideration	Measurement Technique
Size, size distribution	Influences particle's ability to penetrate respiratory system, e.g., [15]	Dynamic Light Scattering (DLS) Condensation Particle Counter (CPC)
Shape	Effects largely unknown [10], but can influence cytotoxicity, e.g., [16]	Transmission or Scanning Electron Microscopy (TEM, SEM)
Agglomeration state	Shown to influence biodistribution and biological effects [10, 17]	Zeta potential
Solubility	Influences aquatic toxicity of metal oxide nanoparticles [18]	Octanol-water partitioning
Surface area	Can influence proinflammatory activity of particles [19]	Brunauer–Emmett–Teller (BET) analysis
Porosity	Link to health effects largely unknown, but can influence surface area (see above)	BET analysis, Atomic Force Microscopy (AFM)
Surface chemistry	Surface reactivity can influence biological responses to certain minerals [20]	Spectroscopy (X-ray photoelectron, Energy dispersive X-ray (EDX)
Impurities, contaminants	Shown to influence aquatic toxicity of some carbonaceous nanomaterials [21]	
Chemical composition	Chemical composition can influence biological potency [22]	ICP-MS, EDX
Density	Influence partitioning and remediation of contaminants in groundwater [23]	Mass/volume comparison
Conductivity	Strong correlations exist between specific conductance and aquatic toxicity [24]	Conductivity meter (e.g., Hach), resistance meter
Crystal structure/crystallinity	Crystallinity may be an indicator of the specific toxicity of certain minerals [25]	X-ray crystallography, Hi-res TEM

Containment

Engineered nanomaterials obtained from commercial suppliers or those prepared in-house at ERDC facilities should be stored in containers that are sufficient to prevent their unintended release during storage, general handling, or shipping. Table 8 summarizes ASTM recommendations for the characteristics of containers for engineered nanomaterials [14].

Table 8. Characteristics of containers for nanoscale materials as adapted from ASTM [14].

- Rigid
- Non-porous
- Tightly sealing, leak-tight
- Made of compatible materials
- Smooth surfaces, such as plastic containers, metal drums, or fiber drums coated internally
- Of appropriate strength and construction to maintain integrity during reasonably foreseeable mishandling while full

Examples of containers frequently used for laboratory containment of some common engineered nanomaterials are summarized below in Table 9.

Table 9. Examples of containers used in certain applications to contain engineered nanomaterials in the laboratory.

Application	Example	Image
Storage of dry nanopowders, such as carbon nanotubes, in a tightly sealed, photo-resistant container	Amber wide-mouth packer with polyvinyl-lined closures. Amber glass aids in storing light sensitive powders. **Source:** www.fishersci.com	
Containment of liquid nanoparticle suspensions, such as solubilized fullerenes or gold and silver colloids.	Amber narrow-mouth boston round bottle with polytetrafluoroethylene liners. Amber glass aids in storing light-sensitive liquids. **Source:** www.epscientific.com	

Product Information: Labels and MSDS (or SDS)

All engineered nanomaterials shipped to ERDC or prepared and stored on-site at ERDC facilities should be identified by appropriate labels and accompanied by an accurate and up-to-date Material Safety Datasheet (MSDS) or Safety Datasheet (SDS).

Labels. Labels should be affixed to any vessel used to contain engineered nanomaterials during on- or off-site shipping and/or long-term storage. Table 10 lists items (and relevant examples) that should be included on product labels. These items are adapted from DOE NSRC [26]. Labels should clearly indicate whether contents include engineered nanomaterials. The type, form, and any known hazards should be identified. A point of contact knowledgeable in the nature of the material should be provided.

Table 10. Items to include on containers with engineered nanomaterial contents. An example label template is provided at Container Label Template_NANO.

Identified on Label	Example
Indicate contents as 'nano'	*'NANOMATERIAL CONTENTS'*
Type	*'Silver nanoparticles'*
Form	*'Dry powder, aggregated'*
Lot number, if available	Include specific lot number, if available
Mass	Include original mass
Known or possible hazards	*'Avoid breathing, ingestion, contact with skin'*
Receipt date/shelf-life	Include date received and expected shelf-life
Contact	Include name and contact details
Other information	*'Exhibits high reactivity, toxicity'*

MSDS (or SDS). While labels should convey only the most pertinent information necessary to remind an end-user of a material's identify and immediate hazards, the global harmonization standard (GHS) suggests that MSDS (or SDS) should provide more detailed information (see Box 1).

Box 1. What is the GHS Safety Data Sheet (SDS)?

According to the OSHA guide to the The Globally Harmonized System of Classification and Labeling of Chemicals (GHS), the purpose of the (Material) Safety Data Sheet (SDS) is to provide *"comprehensive information for use in workplace chemical management. Employers and workers use the SDS as sources of information about hazards and to obtain advice on safety precautions. The SDS is product related and, usually, is not able to provide information that is specific for any given workplace where the product may be used. However, the SDS information enables the employer to develop an active program of worker protection measures, including training, which is specific to the individual workplace and to consider any measures that may be necessary to protect the environment. Information in a SDS also provides a source of information for other target audiences such as those involved with the transport of dangerous goods, emergency responders, poison centers, those involved with the professional use of pesticides and consumers."* **Source:** www.osha.gov/dsg/hazcom/ghs.html#4.0

Table 11 lists the safety datasheet requirements under the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) adopted by the United Nations [27]. There has been much discussion, both in the US and internationally, regarding the GHS and the exact items (and their order of occurrence) to include on safety datasheets (MSDS or SDS). This information is subject to change and users of this guide should take any necessary precautions to ensure that they are in compliance with all applicable institution, local, state, and federal guidelines pertinent to hazard communication. While every effort should be made to complete all of the information included on the MSDS or SDS, it is likely that not all information will be available to do so. If certain information is not known, then this should be stated—*information should not be extracted from equivalent materials at the bulk-scale given that physical and chemical properties of engineered nanomaterials may differ dramatically from bulk-scale materials having similar chemical composition.* For samples, however, DOE NSRC [26] suggests that researchers should prepare a document *"that describes known properties and other properties that deem reasonably likely to be exhibited by samples"*.

Table 11. Items to include on GHS safety datasheets [27]. An example GHS safety datasheet (or MSDS) is provided at MSDS Template_NANO.

▪ Identification
▪ Hazard identification
▪ Composition/information on ingredients
▪ First aid measures
▪ Firefighting measures
▪ Accidental release measures
▪ Handling and storage
▪ Exposure controls/personal protection
▪ Physical and chemical properties
▪ Stability and reactivity
▪ Toxicological information
▪ Ecological information
▪ Disposal considerations
▪ Transport information
▪ Regulatory information
▪ Other information

Shipping

According to DOE NSRC [26], all personnel tasked with shipping and receiving engineered nanomaterials to off-site destinations should be current on HazMat Employee training required by 49 CFR Subpart H. Untrained individuals needing to ship engineered nanomaterials should consult with a member of their organization who has received the necessary training. In addition, the DOE NSRC [26] suggests that packaging of engineered nanomaterials for shipping should comply with Packing Group I—*"substances presenting high danger"*—as per United Nations Model Regulations [28], and include secondary containment and absorbent packing materials, such as vermiculite or cellulose to protect interior packaging from damage or to absorb liquids that might leak during normal transport. As illustrated by the example in Figure 2, these types of packages can be prepared easily by either individual investigators or shipping managers.

Internal container (e.g., 11 ml threaded glass vial)	**Secondary Container (e.g., 125 ml wide-mouth bottle)**	**If Liquid, Add Sorbents (e.g., loose sorbent)**	**Final Packaging**

e.g., Cat. No. 03-339-25D	*e.g., Cat. No. 02-896-1C*	*e.g., Cat. No. 18-999-2540*	*Various*

Figure 2. Preparation of nanoparticles for shipment. The actual nanoparticle sample is usually contained in a tightly capped, threaded glass vial. The vial can then be placed in a secondary container, such as a wide-mouth plastic bottle. If the sample is in liquid form, then loose sorbent materials can be added around the vial inside the plastic bottle. The plastic bottle can then be placed in a labeled package (e.g., cardboard) for final shipping. Note: The example products shown here are from www.thermofisher.com[1].

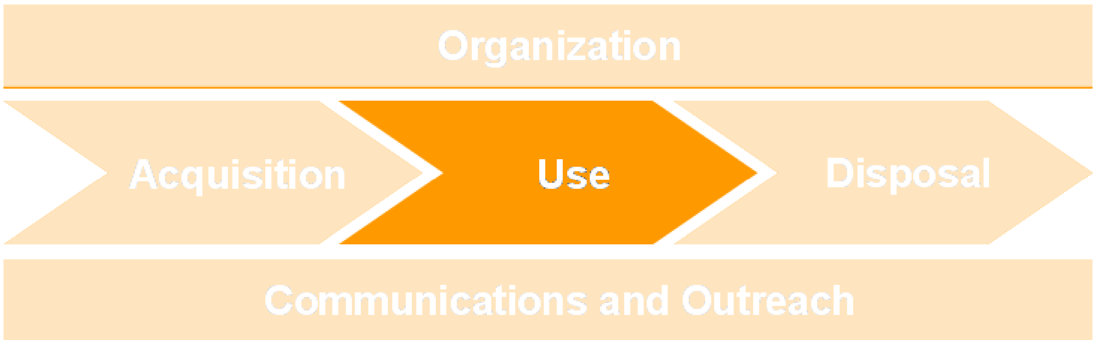
Action Items

The following summarizes action items from this section:

- ☐ Establish NMIL and minimum requirements for nanomaterial products obtained from external suppliers
- ☐ Establish review process for on-site preparation of engineered nanomaterials
- ☐ Effectively characterize all engineered nanomaterials as part of an overall hazard evaluation program

[1] Use of trade names does not constitute endorsement by the federal government.

- ☐ Follow ASTM guidelines for storage of engineered nanomaterials in appropriate containers
- ☐ Ensure that product labels and MSDS (or SDS) are accurate and GHS compliant
- ☐ Follow appropriate shipping guidelines for packages containing engineered nanomaterials (UN Packing Group I designation); consider using secondary containers and sorbents



<u>Use.</u> The following summarizes SOPs for the use of engineered nanomaterials at ERDC facilities.

In this section:

- ☐ Overview
- ☐ Applicable Standards
- ☐ Facility Access
- ☐ Personnel Training
- ☐ Engineering Controls
- ☐ Personal Protective Equipment
- ☐ Medical Screening
- ☐ Workplace Monitoring
- ☐ Maintenance and House-keeping
- ☐ Clean-up of Spills
- ☐ On-site Storage of Engineered Nanomaterials
- ☐ ERDC Case Study: Results of initial assessment by NIOSH Field Team
- ☐ Task-specific Guidance
- ☐ Action Items

Overview

Effective mitigation of nanotechnology EHS risks in the workplace requires a multi-pronged strategy to promote awareness of applicable standards, limit access to facilities where engineered nanomaterials are handled, training workers in safe handling procedures, devise multi-tier protective strategies, provide for voluntary medical screening, and validate control strategies through periodic monitoring of the nanotechnology workplace. This section provides guidance for developing and implementing procedures that minimize nanotechnology EHS risks during use of engineered nanomaterials at ERDC facilities.

Applicable Standards

Based on the Occupational Safety and Health Administration (OSHA) nanotechnology topic webpage [29], Table 12 lists examples of standards that may be applicable in situations where employees are exposed to engineered nanomaterials. On-site ERDC facility EHS managers or contracted EHS personnel should be familiar with these standards, their applicability to engineered nanomaterials, and their implementation.

Table 12. OSHA standards that may be applicable in situations where employees are exposed to engineered nanomaterials.

- 1904, Recording and reporting occupational injuries and illness [Recordkeeping]
- 1910.132, Personal protective equipment [Personal Protective Equipment]
- 1910.133, Eye and face protection [Eye and Face Protection]
- 1910.134, Respiratory protection [Respiratory Protection]
- 1910.138, Hand protection
- 1910.141, Sanitation
- 1910.1200, Hazard communication [Hazard Communication]
- 1910.1450, Occupational exposure to hazardous chemicals in laboratories [Laboratories]
- Certain substance-specific standards (e.g., 1910.1027, Cadmium) [Cadmium]

Facility Access

Access to laboratory areas where engineered nanomaterials are handled or stored should be restricted to prevent the likelihood of an untrained end-user accessing engineered nanomaterials. The extent of restriction may range from signage to secured labs, dependent on the hazards posed by the material. Table 13 breaks out facility access restrictions into two classes: 1) ‘minimum’ restrictions, which should be present at any facility where nanomaterials are used and 2) ‘potential’ restrictions, which, in addition to minimum restrictions, may be needed based on consideration of a nano-specific hazard assessment.

Table 13. Summary of ‘Minimum’ and ‘Potential’ facility access restrictions. ‘Minimum’ restrictions are to be applied to all laboratories where nanomaterials are stored or used. ‘Potential’ restrictions may be required upon consideration of a nano-specific hazard assessement.

Minimum	Potential
✓Locate away from general use areas (e.g., cafeteria) ✓Signage indicating *‘Nanomaterial Usage Area’* ✓Basic entry locks ✓Training for all facility users in specific nano hazards ✓Authorized users only	✓Badge-access entries ✓Specialized containment locks ✓Re-locate facility away from general facilities

Personnel Training

Nanotechnology-specific safety training should be provided for any individual who works with (or may come in contact with) engineered nanomaterials. At a minimum, this training should involve familiarizing personnel with general classes of engineered nanomaterials, particularly those classes that are routinely handled at ERDC facilities. Workers should be made aware of general hazards posed by these substances as well as any available protective measures. If results are available for risk assessments, monitoring, or health surveillance, then this information should be shared with the worker in a straightforward manner. It should be made clear, however, that worker adherence to a well-designed safety program based on general laboratory safety practices should offer a high-degree of protection.

According to the British Standards Institute (BSI) *Guide to Safe Handling and Disposal of Manufactured Nanomaterials* [30], it is recommended that at minimum, workers should be provided the information listed in Table 14 (paraphrased from document).

Table 14. Information to be provided to nanotechnology workers.

- Names and possible health risks of substances to which they may be exposed
- Applicable exposure limits
- Relevant safety data, such as that contained in a Material Safety Data Sheet (MSDS)
- Significant risk assessment findings
- Precautionary measures to protect themselves and co-workers
- Monitoring results, particularly those exceeding applicable exposure limits
- Health surveillance results

The Department of Energy Nanoscale Science Research Centers' *Approach to Nanomaterial ES&H* [26], outlines general working practices associated with handling engineered nanomaterials (Table 15). These practices could provide the foundation for development of a personnel training program for mitigation of nanotechnology EHS risks when performing routine tasks.

Table 15. General working practices identified by DOE NSRC [26].

- Transferring engineered nanomaterials in closed, labeled containers
- Taking reasonable precautions to minimize skin contact with engineered nanomaterials
- Implement appropriate alternative work practice controls when handling of engineered nanomaterials outside of typical exposure controls is required
- Handling of nanomaterial wastes in accordance with hazardous chemical waste guidelines
- HEPA vacuum-cleanup of dry engineered nanomaterials in accordance with established policies and procedures

The nature of nanotechnology-specific training is likely to vary greatly among differing laboratories. Consequently, the exact nature of any training provided should be aligned to the types of tasks that personnel are likely to perform in a given facility or laboratory.

Engineering Controls

According to NIOSH [31], well-maintained controls such as source enclosures and local exhaust ventilation should offer protection against exposures to engineered nanoparticles. Enclosures are especially important for work practices requiring handling of engineered nanoparticles in dry powder form (e.g., weighing, mixing, etc.). Features listed in Table 16 are thought to offer added protection against exposures to engineered nanoparticles.

Table 16. Features of enclosures thought to offer added protection against exposures to engineered nanoparticles.

Feature	Rationale
Low-velocity air flow	Minimizes inadvertent aerosolization of dry forms of engineered nanoparticles
HEPA/ULPA filtration	Based on current knowledge, should effectively capture engineered nanoparticles
Safe filter change-out systems	Minimize exposures to engineered nanomaterials during maintenance
Clean-out access	Minimizes the accumulation of nanoscale particles within exhaust systems

Currently, one enclosure product is available that is specifically marketed as having been tested for efficacy with engineered nanoparticles (Figure 3—see Labconco XPert Nano® Enclosures at: www.labconco.com/_Scripts/editc25.asp?catid=471).[2] A summary report on performance testing of the unit with a 23 nm (average diameter) silicon dioxide aerosol challenge is available at www.nanosafeinc.com/Nanotech_Register.html.

Figure 3. Labconco XPert Nano® Enclosures are used to contain hazardous powders and particulates generated during nanoparticle manipulation and dry powder chemical handling.

[2] Use of trade names does not constitute endorsement by the US government).

Personal Protective Equipment

Data is limited on the effectiveness of conventional personal protective equipment (PPE) against engineered nanoparticles. According to NIOSH [31], it is recognized that protective clothing (e.g., gloves, fabrics, suits) is limited in its effectiveness to mitigate dermal exposures and additional laboratory research is needed to determine penetration efficiencies of engineered nanoparticles through conventional protective clothing. Similarly, NIOSH notes that little is known about either the permissible exposure limits for aerosolized engineered nanoparticles or the effectiveness of conventional respirators against them, and that additional studies are needed to determine nanoparticle collection efficiencies for NIOSH-certified respirators. However, NIOSH notes that the decision to institute a respirator protection program should be based on a combination of factors including professional judgment and hazard assessment results. To assist with this process, NIOSH has published a document entitled, NIOSH Respirator Selection Logic (RSL), which is available online at www.cdc.gov/niosh/docs/2005-100/default.html.

Until more definitive evidence is available, some organizations, such as the Department of Energy (DOE) Nanoscale Science Research Centers (NSRC), have published voluntary guidelines (Table 17) it uses for protecting laboratory personnel against nanoparticle exposures [26].

Table 17. DOE NSRC voluntary guidelines for PPE.

- Wear PPE in conjunction with engineering controls, so as to provide multiple levels of protection
- Perform a hazard evaluation (as per 29 CFR 1910) to select appropriate PPE
- Include use of the following PPE in a typical wet-chemistry laboratory environment:
  - Closed-toed, low-permeability shoes (may include over-the-shoe booties)
  - Long pants (no cuffs)
  - Long-sleeved shirt
  - Laboratory coat (no cuffs)
  - Gauntlet-type or nitrile gloves with extended sleeves
    - Consider chemical resistance of material
    - Change gloves routinely and/or 'double glove'; to eliminate exposed wrists, extend glove to overlap cuff of lab-coat
    - Keep contaminated gloves in sealed containers
    - Wash hands, forearms after wearing gloves
  - Eye protection (e.g., safety glasses, face shields, goggles; appropriate for hazard)
  - Respirators (protection level of half-mask, P-100 cartridge-type or greater)

Figure 4 provides a simple schematic that can be posted in laboratories and workspaces to rapidly communicate the specific types of PPE that can be worn to help reduce EHS risks when handling engineered nanomaterials.

GOAL. Control nanomaterial exposures to "as low as is reasonably practicable." [14]

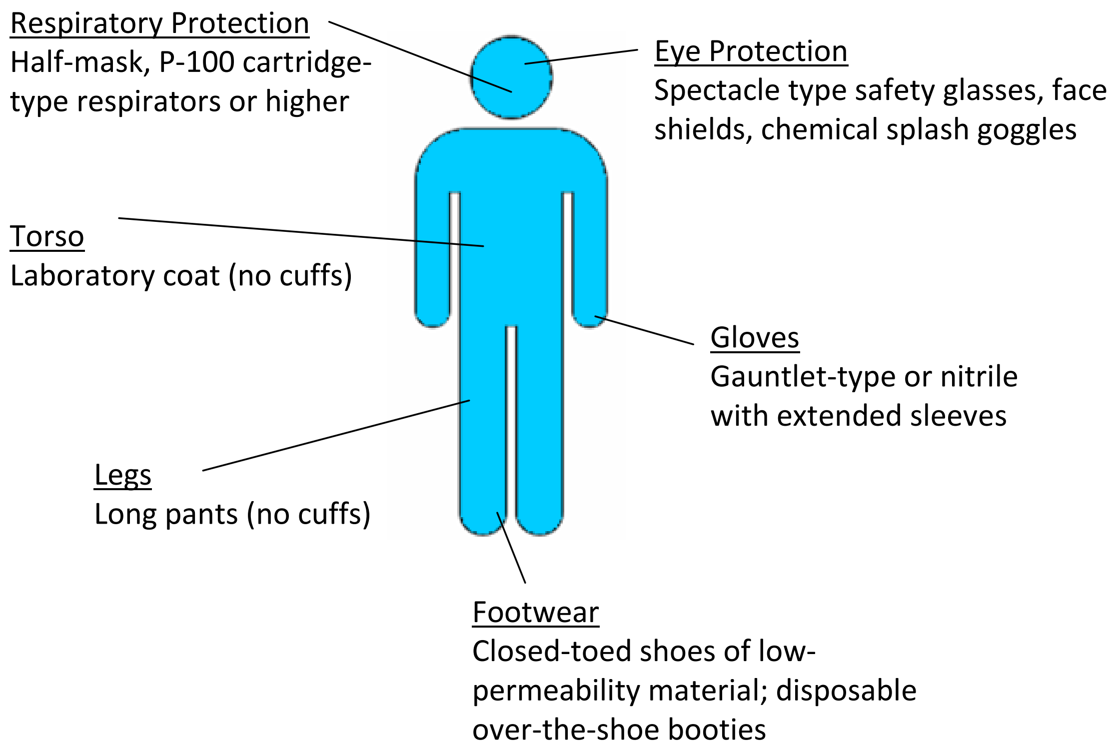


Figure 4. Overview of PPE that has been considered by other organizations for use when handling engineered nanomaterials.

Medical Screening

Studies of the toxicology of select engineered nanomaterials and epidemiology of individuals exposed to incidental nanoparticles suggest that it is prudent to employ precautionary measures to protect workers who may be exposed to engineered nanomaterials [32]. Recently, the National Institute for Occupational Safety and Health (NIOSH) published interim guidance ([32]) concerning the appropriateness of medical screening for asymptomatic workers who may be exposed to engineered nanomaterials. The document notes that only interim guidance is available at this time as current scientific and medical evidence is insufficient to recommend a specific medical screening strategy for potentially exposed workers. Interim recommendations are summarized in Table 18.

Table 18. Interim medical screening recommendations from NIOSH [32].

- Medical screening should be considered only one part of a concerted safety strategy.
- Take prudent measures to control workers' exposures to nanoparticles.
- Conduct hazard surveillance as the basis for implementing controls.
- Consider established medical surveillance approaches to help assess whether control measures are effective and identify new or unrecognized problems and health effects.

The DOE NSRC [26] guidelines provide additional suggestions for medical screening, such as offering (with the opportunity for exemption) baseline medical monitoring including, for example, urinalysis, blood chemistry, and pulmonary function. Baseline and periodic medical screening has been suggested as a component of the NanoSafe™ framework, an industrial nanotechnology EHS risk management framework [33]. As noted by ASTM [14], however, such programs should be developed and implemented in consultation with appropriate medical, legal, and industrial hygiene professionals.

Workplace Monitoring

Workplace exposures to engineered nanomaterials may occur via inhalation, ingestion, dermal contact (with the materials themselves or with surfaces contaminated with the materials such as countertops or PPE), or through the eyes and mucus membranes [14]. Actual exposure routes will be dependent on the physical characteristics (e.g., solid powder, liquid suspension) of the nanomaterials and handling requirements encountered in a particular workplace.

Inhalation and dermal exposures are currently of greatest concern given the ease with which some dry nanomaterials may become aerosolized or accumulate on work surfaces [31]. Consequently, several workplace monitoring programs have been reported for characterizing particulate emissions and surface contamination during nanoparticle handling. Such programs may be developed and implemented in-house (assuming expertise is sufficient to do so) or in conjunction with a qualified provider of workplace particulate monitoring services. With regards to the latter, NIOSH has assembled a highly trained Field Research Team (see www.cdc.gov/niosh/docs/2008-120/) that can assist facilities with monitoring nanotechnology workplaces on a voluntary basis. Regarding the former (development of an in-house workplace monitoring program) possible approaches have been developed and reported by representatives of government and industrial laboratories. Table 19 summarizes, in the context of ERDC facilities, a workplace monitoring program developed by DOE NSRC for characterization of aerosolized nanoparticles. Refer to [26] for a complete version of the monitoring program. A monitoring program applied in a carbonaceous nanomanufacturing environment is described by Yeganeh et al [34].

Table 19. Summary of a nanotechnology workplace monitoring program described by DOE NSRC [26].

Purpose

To characterize emissions of engineered nanomaterials (1-100 nm) as a result of nanoscale research performed at ERDC facilities.

Instrumentation/Equipment

(Note: instruments require operation by a trained end-user; listing of specific instrument models does not constitute endorsement by the federal government)

- TSI Model 3007 Condensation Particle Counter (CPC)
- GRIMM Model 1.108 SubMicron Aerosol Spectrometer (SAS)
- Scanning or Transmission Electron Microscope (SEM/TEM) with Energy Dispersive X-ray Spectrometer (EDX)
- Conventional Video/Photo Capture Equipment

Protocol

(Note: protocol assumes target sampling areas have already been established based on the presumption that a particular activity or process may aerosolize engineered nanoparticles)

- Repeat the following measurements for background ambient conditions and at various points in the workplace before, during, and after the performance of targeted activities/processes
- Measure total particulate concentration (particles/cubic centimeter) using TSI CPC
- Measure particle size distribution (particles/liter) using GRIMM SAS
- Characterize particle morphology and chemical composition using SEM/TEM with EDX
- Take detailed field notes and electronic images to document laboratory activities and processes as a basis for control and/or documentation

Permissible exposure limits for engineered nanoparticles are currently unknown, but examples of interim limits may be found in reports by NIOSH [32], ASTM [14], and BSI [30]. It is important to note, however, that these interim limits were established from conventional particulate exposures and have not been shown to afford any protection against engineered nanoparticles. Nevertheless, it is important that monitoring of the workplace be performed to ensure compliance with existing particulate standards and to quantify the extent to which personnel are exposed to particulates in general, and engineered nanoparticles in particular.

Workplace Maintenance and Housekeeping

Routine maintenance and housekeeping are important to ensure the proper function of engineering controls, to prevent the accumulation of engineered nanomaterials on surfaces or in areas such as ductwork, and to reduce accidental exposures. The following sections summarize general maintenance and housekeeping procedures to minimize nanotechnology EHS risks in the workplace.

Ventilation System Cleanliness. Explosion hazards have been associated with the accumulation of fine organic and inorganic particles, and similar hazards are likely to exist for engineered nanopowders [35]. Further, re-aerosolization of particles or contact with skin, can create respiratory and dermal hazards, respectively [26, 31]. Areas that may accumulate fine dust and debris, such as heavy-use surfaces, air-handling ductwork and suspended ceilings should be inspected frequently to facilitate the timely removal of accumulated materials, particularly fine powders. Explosion risks of materials should be determined, as well as the potential for cross-reactivity with other chemicals, elevated temperatures, or other relevant environmental factors. A certified industrial hygienist can assist with identifying and minimizing explosion hazards.

Functioning of Engineering Controls. Protective devices such as enclosures, fume hoods, or gloveboxes, which are intended to minimize worker exposures to chemicals, materials, and/or biological agents, should be routinely inspected and maintained to ensure their proper function. Since information on permissible exposure limits is lacking for engineered nanomaterials, minimization of exposures through effective control devices should be made a top priority of health and safety managers. It is important to note that during maintenance activities such as enclosure filter change-out and vacuum-cleaning of ductwork, workers (both those directly involved in the activity AND those who may be working nearby) may be at increased risk for exposure to engineered nanoparticles. Additional PPE, specialized equipment, or modified work practices may be necessary to minimize these increased exposure risks.

General Housekeeping. General housekeeping procedures are described by the DOE NSRC [26] and are outlined in Table 20.

Table 20. General housekeeping procedures described by DOE NSRC [26].

- Minimize contact with working surfaces
- Use moist disposable wipes to clean working surfaces as needed or at the end of each shift
- Use inert cleaning agents
- For dry materials use approved HEPA vacuums followed by wet-wiping
- Do NOT use sweeping or compressed air
- Dispose of contaminated materials (e.g., wipes) as described in the 'Disposal' section of this document

Clean-up of Spills

Spills of engineered nanomaterials should be cleaned up promptly. General procedures for clean-up of engineered nanomaterial spills are described by DOE NSRC [26] and are outlined in Table 21.

Table 21. Spill clean-up procedures described by DOE NSRC [26].

- Restrict access to spill and initiate clean-up promptly
- Consider contacting a trained HazMat crew
- Refer exposed personnel for medical evaluation
- Use tacki walk-off mats to reduce tracking/spread of spilled materials
- Use moist disposable wipes to clean working surfaces as needed or at the end of each shift
- Use inert cleaning agents
- For dry materials, use approved HEPA vacuums followed by wet-wiping
- Do NOT use sweeping or compressed air
- Consult MSDS for any material-specific guidance regarding spills
- Dispose of contaminated materials (e.g., wipes) as described in the 'Disposal' section of this document
- Document the type and amount of the spill along with any exposed personnel

While hazard information for most nanoparticle-containing products is limited, it may be of practical benefit to designate spills of nanoparticles as either 'minor' or 'major' depending on a number of factors such as the magnitude of the spill, toxicity of the spilled material, and potential for nanoscale particles to be mobilized from the spill. It is important to note, however, that it may be necessary to consider factors other than those listed here. Ultimately, product labels and safety datasheets provided by generators of these materials should provide more specific information on spill management. Table 22 illustrates examples of a 'minor' and 'major' spill as well as a response strategy and rationale for each.

Table 22. Example 'minor' and 'major' spills of engineered nanomaterials along with a possible response strategy and rationale for each.

	'Minor' Spill	'Major' Spill
Example	Spill of milliliter-volume of liquid gold nanoparticle suspension onto an isolated laboratory bench-top	Spill of multi-gram quantities of carbon nanotubes or quantum dots in a heavy-traffic laboratory area.
Response Strategy	✓Initiate clean-up promptly ✓Use moist disposable wipes to clean working surfaces ✓Use inert cleaning agents ✓Consult MSDS for any material-specific guidance regarding spills ✓Dispose of contaminated materials (e.g., wipes) as described in the 'Disposal' section of this document	✓Restrict access to spill and initiate clean-up promptly ✓Consider contacting a trained HazMat crew ✓Refer exposed personnel for medical evaluation ✓Use tacki walk-off mats to reduce tracking/spread of spilled materials ✓For dry materials, use approved HEPA vacuums followed by wet-wiping ✓Do NOT use sweeping or compressed air ✓Consult MSDS for any material-specific guidance regarding spills ✓Dispose of contaminated materials (e.g., wipes) as described in the 'Disposal' section of this document ✓Document the type and amount of the spill along with any exposed personnel
Rationale	**Magnitude** = Small (milliliter volume) **Toxicity** = Low (gold nanoparticles) **Mobility** = Low (in liquid) **Exposure** = Low (controlled bench top)	**Magnitude** = High (multi-gram quantities) **Toxicity** = Unknown (nanotubes) **Mobility** = Moderate to High (powder form) **Exposure** = High (high traffic area)

On-site Storage of Engineered Nanomaterials

In general, on-site storage of engineered nanomaterials (and associated wastes) should be kept to a practical minimum. If on-site storage of large quantities of these materials is required, then efforts should be taken to ensure that this is done under safe conditions (e.g., appropriate containment, temperature, light exposure, distance from reactants). Further, health and safety managers as well as emergency personnel should be made aware of the location of these storage sites, the nature of materials present, and any other pertinent information. Table 23 summarizes important considerations for on-site storage of engineered nanomaterials and associated waste products.

Table 23. General guidance for on-site storage of engineered nanomaterials and wastes.

- Designate secure, low-traffic areas for storage
- Provide signage to indicate the presence of engineered nanomaterials and wastes, and limit or restrict access
- Designate a responsible party to oversee a particular collection area or group of collection areas (provide contact information for the POC)
- Use containers that meet ASTM-suggested criteria
- Label containers as to their nanomaterial components
- Store containers inside a fume hood or source-enclosure
- In general, store nanomaterials and wastes in a cool, dry areas; for solvent-laden wastes, make sure area is well-ventilated
- Follow specific storage recommendations specified on safety datasheets
- Avoid mixing incompatible materials as this can increase the risk of explosion or fire (consult a professional industrial hygienist to determine the compatibility of different materials)

ERDC Case Study: Results of initial assessment by NIOSH Field Team

A summary report by the NIOSH Nanotechnology Field Team was delivered to ERDC on June 12, 2008, following NIOSH's assessment of ERDC nanotechnology facilities (refer to NIOSH Letter report US Army COE Vicksburg June 2008). The report provided results of the initial assessment as well as recommendations for improving ERDC work practices that should contribute to the evolving worker health and safety program at ERDC. The recommendations were based on observations and interactions of the NIOSH Nanotechnology Field Team with ERDC personnel.

Materials in use at time of assessment. The following materials were in-use during the time that the field assessment was performed by NIOSH (Table 24).

Table 24. Nanomaterials in use at ERDC facilities during time of NIOSH Nanotechnology Field Team assessment.

- Fullerene (C_{60}): purity 99.5+%, catalog # 600-9950, Lot #BT-6947; SES Research, Houston, TX.
- Raw Multi-Walled Carbon NanoTubes (Raw-MWCNT): Outside Diameter = 10-20 nanometers (nm); length = 10-30 micrometers (µm), purity >95 wt%, Cheap Tubes, Inc., Brattleboro, VT.
- Functionalized (Hydroxylated) Multi-Walled Carbon NanoTubes (MWCNT-OH): Outside Diameter = 20-30 nm; length = 10-30 µm, purity >95 wt%, Cheap Tubes, Inc., Brattleboro, VT.
- Carbon Black: amorphous carbon, average primary particle size of 15 nm; Printex 95 brand product from Evonik North America, Parsippany, NJ.

Work Practices Evaluated. The goal of the assessment by the NIOSH Nanotechnology Field Team was to evaluate ERDC nanomaterial process and handling techniques and determine whether engineered nanomaterials were released to the laboratory atmosphere, which could result in potential worker exposure. In addition, if a release of nanomaterial were detected, the laboratory staff requested that NIOSH provide consultative guidance on procedures that could be implemented to control such releases. Table 25 summarizes the types of processes and work practices that were evaluated during the NIOSH assessment.

Table 25. Processes and work practices evaluated during NIOSH Nanotechnology Field Team Assessment of ERDC laboratories.

Process/Work Practice	Description
Weighing 4 to 200 milligrams (mg) on an electronic balance and transfer of nanomaterials to water-containing beaker sitting atop a magnetic mixing apparatus.	This procedure was performed inside a laboratory fume hood with the hood air handler temporarily turned off and the sash open halfway.
Sonicating approximately 20 milliliters (ml) of previously mixed nanomaterials for 20 minutes inside a Branson Sonifier model 450.	This benchtop unit is housed within an unventilated plastic enclosure and was operated at a 40% duty cycle.
NOTE. Personal protective equipment (PPE) worn by workers when performing weighing/transfer tasks and sonication processes consisted of a cotton laboratory coat, latex gloves, and an N95 filtering facepiece respirator.	

Measurement Methods. As described in the NIOSH report, *"two direct-reading, real-time instruments were used to characterize process emissions and determine the number concentration of emitted airborne particulate during various processes and handling procedures. The sampling inlet of each instrument was positioned as close as possible to the suspected point of emission for a given process."* Filter-based air samples were also collected to facilitate analysis of particulate matter by transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS). Details on the exact nature of the measurement instruments and filter-based sampling work is contained in the NIOSH report.

Observations and Recommendations. Table 26 summarizes observations and recommendations from the report prepared by the NIOSH Nanotechnology Field Team following their assessment of ERDC facilities in 2008.

Table 26. Observations and recommendations from NIOSH Nanotechnology Field Team Report prepared for ERDC in 2008.

Observation	Recommendation
Currently, there are no occupational exposure limits specific to engineered nanomaterials.	It is good occupational safety and health practice to keep exposures to new and uncharacterized materials as low as possible. Since the air sampling data indicates that some release of the material occurred, it would be prudent to attempt to control such releases to avoid exposure.
The fume hood ventilation system was turned off during weighing and transferring materials because the hood air velocity (measured at 100 feet per minute at the face) was high enough to result in loss of material during the transfer from the material container to the analytical balance.	To avoid this problem and better control emissions during this process, a low air flow analytical balance enclosure equipped with a High Efficiency Particulate Air (HEPA) filtered exhaust could be used. Such a unit is commercially available from a variety of manufacturers.
Despite being housed inside an enclosure, the sonicator has the potential to emit engineered nanomaterial when the enclosure door is opened after the sonication process is complete.	It would be prudent to relocate and use the sonicator inside a properly operating laboratory fume hood. If a release occurs during the opening of the sonicator enclosure door, the laboratory fume hood should prevent the engineered nanomaterials from escaping into the room. However, the effectiveness of this arrangement will need to be evaluated to ensure that adequate capture of any release is achieved.

Further Task-Specific Guidance

As nanotechnology-specific work increases in ERDC laboratories, monitoring and subsequent management of possible exposures in the workplace, as well as unintended releases to the natural environment become increasingly complex. Consequently, it is expected that task-specific guidance will need to be developed for ERDC facilities and personnel as new nanotechnology-related activities are undertaken and new information on hazards and exposure risks becomes available.

Table 27 lists tasks identified by NIOSH [31] as general workplace procedures that may increase the risk of exposure to nanoparticles.

Table 27. Workplace tasks listed by NIOSH that may increase the risk of exposure to engineered nanomaterials.

- Working with nanomaterials in liquid media without adequate protection (e.g., gloves) will increase the risk of skin exposure.
- Working with nanomaterials in liquid during pouring or mixing operations, or where a high degree of agitation is involved, will lead to an increase likelihood of inhalable and respirable droplets being formed.
- Generating nanoparticles in the gas phase in non-enclosed systems will increase the chances of aerosol release to the workplace.
- Handling nanostructured powders will lead to the possibility of aerosolization.
- Maintenance on equipment and processes used to produce or fabricate nanomaterials or the clean-up of spills or waste material will pose a potential for exposure to workers performing these tasks.
- Cleaning of dust collection systems used to capture nanoparticles can pose a potential for both skin and inhalation exposure.
- Machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles can potentially lead to aerosolization of nanomaterials.

More specifically, in ERDC laboratories, certain routine tasks, such as those listed in Table 28, may increase the likelihood of ERDC personnel to be exposed to engineered nanomaterials. Typically, engineered nanomaterials will arrive from suppliers as aggregated dry powders. Common practice involves suspending these dry materials in aqueous or solid (e.g., sediment) media. Given that this practice requires handling of the dry materials, aerosolization of nanoscale particles may occur. Aerosolized particles pose respiratory hazards that should be carefully managed, particularly when high aspect ratio materials such as carbon nanotubes are handled. Clean-up of laboratory surfaces (e.g., benchtops) and test media (e.g., nanoparticle-exposed water, sediment, tissue) may also increase the risk of personnel exposures to engineered nanoparticles.

Table 28. Routine tasks in ERDC laboratories that may expose laboratory personnel to engineered nanomaterials. Subsequent sections summarize protocols for minimizing exposures to engineered nanomaterials.

▪ General Handling (Table 29)
▪ Weighing and mixing with water or sediment (Table 30)
▪ Replacement of water during an exposure (Table 31)
▪ Decontamination of nanomaterial contaminated items and test media (Table 32)
▪ Disposal of contaminated items and test media (next section)

Tables 29-32 offer specific guidelines for minimizing exposures to engineered nanomaterials while accomplishing tasks generally considered routine in ERDC laboratories.

Table 29. General Handling of engineered nanomaterials.

▪ Avoid skin contact with materials and wear protective clothing: laboratory overcoat, gloves and goggles (see previous discussion of Engineering Controls and PPE). Note that some types of nanomaterials have been demonstrated to penetrate laboratory gloves; hence contact with dry powders or solutions containing nanomaterials should be kept to a minimum.
▪ Inhalation of particulate nanomaterials is likely the highest risk of exposure to individuals working with nanomaterials. Therefore, dry nanomaterials should only be handled in a suitable laboratory enclosure operating in accordance with manufacturer specifications.
▪ Containers with engineered nanomaterials should only be opened in a suitable enclosure, not in an open space with air currents.

Table 30. Weighing and mixing with water or sediment.

▪ To minimize inhalation of engineered nanomaterials, weigh samples in a suitable enclosure operating at manufacturer-recommended specifications ▪ Transfer samples into a single “stock concentration” chamber containing a specified amount of water (to limit the potential of particles getting into the air). This stock solution containing a specific amount of nanomaterials may then be manipulated (e.g., sonicated) depending on the design of the study. Aliquots of the suspended stock solution containing nanomaterials (e.g., suspended using a stir bar) can then be transferred with a pipette into test chambers (i.e., for water only exposures) or can be spiked into sediment (e.g., for sediment exposures). ▪ After weighing samples and preparation of the stock concentration chamber, close the enclosure and leave the fan running for 1 hour to help remove any air-borne particles of nanomaterials. ▪ Immediately clean surfaces affected by an accidental spill of nanomaterial with water and wipe with paper towel. Dispose of the paper towel in a dry waste container labeled “**Contains Nanomaterials**”. ▪ Any equipment or material that comes in contact with nanomaterials will be stored in a separate container labeled “**Nanomaterial Supplies**” before decontamination as described below (see Table 26).

Table 31. Replacement of water during an exposure.

▪ Beakers with test materials will be put in holding boxes with water circulation holes already tightly sealed and then the boxes transferred to the exposure water bath.   ▪ Collect overflow water from test beakers in the holding boxes to prevent contaminating exposure water bath.   ▪ For sampling (e.g., for water quality analysis), draw water from the exposure beakers with a syringe and transfer the sample into a separate container. Draw subsamples from this container for water analyses and transfer the remaining water into a container labeled "**Contains Nanomaterials**".

Table 32. Decontamination of nanomaterial contaminated items.

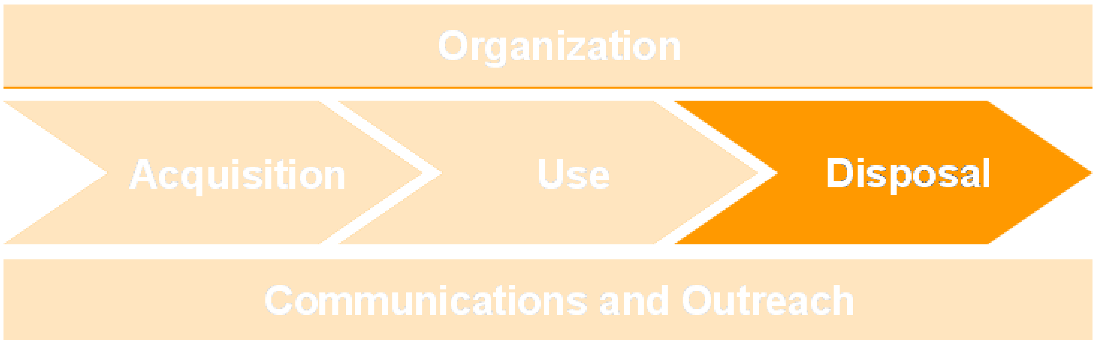
▪ At a minimum, contaminated benchtops should be wet-wiped or HEPA-vacuumed at the end of each shift   ▪ Glassware (and other items) that have come in contact with nanomaterials will be kept in containers (e.g., large plastic containers) separate from other glassware and will be cleaned as soon as possible (ideally, on the same day).   ▪ Contaminated glassware will be first rinsed and scrubbed with deionized water in a ventilated sink, and then placed in the acid bath. The glassware can then be cleaned following conventional laboratory SOPs for cleaning glassware. The brushes will be stored in a container labeled "Nanomaterial Supplies".   ▪ Instruments (e.g., water quality probes) that contact nanomaterials should be washed and rinsed with deionized water in a bucket/basin and the waste water should be stored in a container labeled "**Contains Nanomaterials**". The buckets or basins will be stored in a larger container label "**Nanomaterial Supplies**."

Action Items

The following summarizes action items from this section:

- ☐ Review applicable OSHA standards with an on-site facility EHS manager or qualified professional consultant
- ☐ Restrict access to ERDC laboratories where engineered nanomaterials are handled or stored
- ☐ Implement a nanotechnology-specific training program for personnel who may be exposed to engineered nanomaterials
- ☐ Ensure that engineering controls such as enclosures are available, functioning properly, and used regularly to minimize exposure of personnel to aerosolized nanomaterials
- ☐ Ensure that personnel wear PPE appropriate for tasks involving engineered nanomaterials
- ☐ Implement a voluntary precautionary medical screening program
- ☐ Implement a regular workplace monitoring program aimed at quantifying particulate levels in air and on surfaces; consider use of interim permissible exposure limits described by BSI and ASTM
- ☐ Verify cleanliness of ventilation systems to minimize the accumulation of nanoscale dusts that may pose an explosion hazard
- ☐ Ensure that engineering controls are well-maintained and functioning properly
- ☐ Prepare personnel for elevated risks faced during maintenance such as change-out of enclosure HEPA filters or ventilation system cleaning; plan maintenance in a manner that minimizes unnecessary exposure risks (e.g., perform maintenance during off-hours)
- ☐ Implement general housekeeping procedures to keep working surfaces clean and free of appreciable amounts of engineered nanomaterials
- ☐ Follow general procedures provided for clean-up of spills of engineered nanomaterials
- ☐ Minimize on-site storage of engineered nanomaterials; ensure that storage sites are clearly marked, environmental conditions (e.g., temperature) are appropriate, and appoint a responsible party to oversee the site(s).

- ☐ Follow task-specific guidance when performing common tasks with engineered nanomaterials (e.g., general handling, weighing and mixing, glassware decontamination).
- ☐ Consult a certified industrial hygienist to assist with questions related to the development and implementation of specific workplace procedures that minimize exposures to engineered nanomaterials.



<u>Disposal.</u> The following summarizes SOPs for the disposal of engineered nanomaterials used at ERDC facilities.

In this section:

- ☐ Overview
- ☐ Nanomaterial-bearing Waste Streams
- ☐ Step-wise Process for Disposing of Nanomaterial-bearing Waste Streams
- ☐ Action Items

Overview

While limited information has emerged with respect to management of nanotechnology EHS risks in the workplace (e.g., NIOSH, DOE NSRC), little to no information is available regarding the management of nanomaterial waste streams. This section provides guidance on the disposal of engineered nanomaterials and other items, such as gloves and paper towels, which may become contaminated by nanomaterials during routine handling.

Nanomaterial-bearing Waste Streams

The DOE NSRC nanotechnology EHS guidance document [26] identifies four general types of nanomaterial-bearing waste streams. These streams are identified in Table 33 along with representative examples of each. ERDC personnel tasked with handling or disposing of engineered nanomaterials should become familiar with the different types of nanomaterial-bearing waste streams that they are likely to generate, dispose of, or otherwise encounter.

Table 33. Nanomaterial-bearing waste streams identified by DOE NSRC [26].

Type	Example
Pure	Carbon nanotubes, aluminum oxide powder
Liquid suspensions	Gold nanoparticles in buffer, nanotubes in acidic solution
Nanomaterial-contacted Items	Wipes, gloves, disposable coveralls
Nanomaterial-containing matrices	Composites with potential to leach nanomaterials

Step-wise Process for Disposing of Nanomaterial-bearing Waste Streams

The DOE NSRC nanotechnology EHS guidance document [26] describes a general process for disposing of nanomaterial-bearing waste streams. A step-wise disposal process has been adapted from the DOE NSRC approach and is summarized in Table 34.

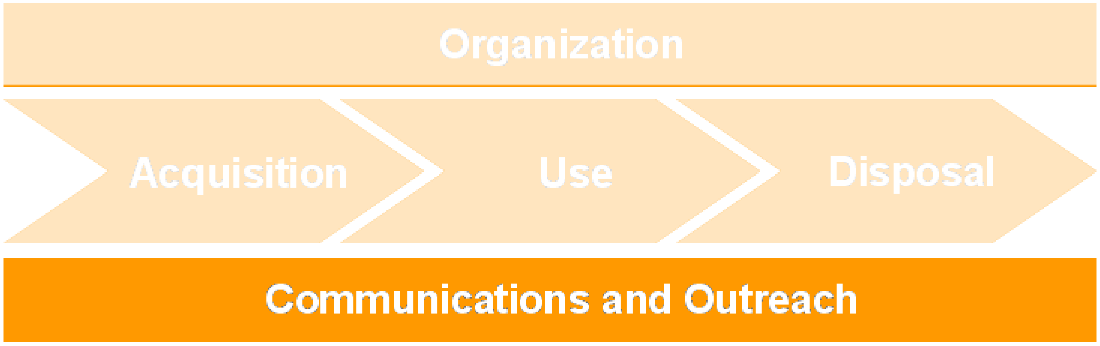
Table 34. Step-wise process for minimizing and managing nanomaterial-bearing waste streams. This step-wise process is based on the DOE NSRC nanotechnology EHS guidance document [26].

Step	Description
1. Minimize	To the extent practicable, the amount of engineered nanomaterials required for a particular task should be minimized. This may include reducing assay volumes, preparing less-concentrated stock suspensions, or stream-lining experimental designs.
2. Avoid	Avoid disposing of pure products in regular trash or down the sink drain. Any sink discharge should be first cleared by an ERDC facility EHS manager or other qualified expert. It is not appropriate to ship wastes off-site for disposal at, for example, partner laboratories.
3. Characterize	Determine whether a particular waste is hazardous or non-hazardous based on requirements in 40 CFR 261.10 to 38, or equivalent state regulations. While not currently required, specialized techniques (e.g., electron microscopy) may be required to effectively characterize some wastes.
4. Package	Nanomaterial-containing wastes should be enclosed in dedicated containers {see 'Acquisition' section for ASTM [14] criteria for containers} that prevent the escape of engineered nanomaterials, and stored in a properly functioning fume hood.
5. Label	Each container used for nanomaterial-bearing wastes should be marked *'Contains Nanomaterials'*. A brief description of the container's contents should be included. Additional information (e.g., responsible party, dates, etc.) may also be included dependent on ERDC policies and procedures.
6. Collection	Loose items (e.g., gloves, wipes, etc.) that have contacted engineered nanomaterials should be stored in a dedicated, re-sealable container and stored in a properly functioning fume hood. Once full, the container may be placed in a secondary container and labeled as to its contents.
7. Processing	Based on results of Step 3 (characterization of waste as hazardous vs. non-hazardous) dispose of packaged/labeled wastes in accordance with ERDC procedures for hazardous or non-hazardous waste.

Action Items

The following summarizes action items from this section:

- ☐ Familiarize ERDC personnel with the types of nanomaterial-bearing waste streams.
- ☐ Avoid disposing of engineered nanomaterials with common trash or down sink drains.
- ☐ Follow step-wise process for disposing of nanomaterial-containing/contacted wastes.



Communications and Outreach. The following summarizes SOPs for communicating nanotechnology EHS risk management activities undertaken at ERDC facilities.

In this section:

- ☐ Overview
- ☐ Internal (ERDC) Communications
- ☐ External Communications
- ☐ Action Items

Overview

The emerging nature of nanotechnology EHS risks requires the exchange of accurate and timely information within and outside of ERDC. This section provides guidance for handling ERDC communications regarding nanotechnology EHS issues both internally and externally.

Internal (ERDC) Communications

Internal ERDC communications include all major communications of nanotechnology EHS information to ERDC personnel tasked with acquiring, using, or disposing of engineered nanomaterials at ERDC facilities. Criteria used to define 'major' internal communications are subject to definition by the originator or distributor of a particular communication, and may take the form of, for example, internal memoranda, significant multi-recipient emails, internal reports, and training programs. Such communications should be reviewed by members of the Nanotechnology EHS Committee and other relevant ERDC personnel (in accordance with established ERDC procedures) prior to widespread internal distribution and documented for record-keeping purposes.

External Communications

External communications include all ERDC-led publications, conferences, symposia, press-releases, memoranda of agreement, and related communications that convey nanotechnology EHS information to the public or other laboratories and agencies. Such communications should be reviewed by members of the Nanotechnology EHS Committee and other relevant ERDC personnel (in accordance with established ERDC procedures) prior to external distribution and documented for record-keeping purposes. A centralized point-of-contact (e.g., one member of the Nanotechnology EHS Committee) should be appointed to facilitate the timely exchange of pertinent nanotechnology EHS information with other laboratories (e.g., other DOD, academic, or commercial laboratories) and government agencies (e.g., USGS, USEPA, NIOSH).

Action Items

The following summarizes action items from this section:

- ☐ Provide for committee-level review of major internal and external communications
- ☐ Document communications for record-keeping purposes
- ☐ Establish a central point-of-contact to coordinate with other laboratories and agencies with respect to the timely exchange of pertinent nanotechnology EHS information

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